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Note

Structure and magnetic properties of a trinuclear nickel(II) complex with benzenetricarboxylate bridge

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ABSTRACT

Novel trinuclear Ni(II) complex $[Ni_3(pmdien)_3(btc)(H_2O)_3](ClO_4)_3 \cdot 4H_2O$, **1** where pmdien = *N*,*N*,*N*′,*N*′,*N*″-pentamethyldiethylenetriamine, H_3btc = 1,3,5-benzenetricarboxylic (trimesic) acid, has been prepared and structurally characterized. Three nickel atoms are bridged by btc trianion and their coordination sphere is completed by three N atoms of pmdien and O atom of the water molecule. The three nickel(II) magnetic centers are equivalent and their coordination spheres are completed to deformed octahedrons. Magnetic susceptibility was measured over the temperature range 1.8–300 K and $zJ' = -0.19\ cm^{-1}$, $D = 3.79\ cm^{-1}$, $g = 2.18$ parameters were calculated.

1. Introduction

A very important class of compounds in both inorganic and bioinorganic chemistry is that containing carboxylato group. Especially, the use of multifunctional ligands for the preparation of metal organic compounds becomes of great interest. The compounds can contain 2D and 3D frameworks linked by organic ligands or hydrogen bonding. The compounds formed can be potentially used for the preparation of inorganic porous materials applicable for adsorption, ion exchange or catalysis.

1,3,5-Benzenetricarboxylic acid ($btcH_3$) is of interest because of its symmetry and potential use of six oxygen donor atoms. Many compounds with different degrees of deprotonation of $btcH_3$ were synthesized. Because of the versatility in bonding properties it is always very important to obtain completely solved crystal and molecular structures. The examples of coordination compounds with uncoordinated btc anions are rather rare as follows from CCDC database [1–4]. A very wide range of compounds involving these with btc bridge were obtained and their structural properties are known. In some cases, the acid is not completely deprotonized and even mononuclear complex or complexes bridged by second ligand can be formed [5–9]. But most of the complexes with btc anion are polynuclear and a variety of coordination modes are observed. These are for example: (a) chelating bis-bidentate and monodentate [10,11]; (b) chelating-bridging bis-bidentate and chelating bidentate [12]; (c) monodentate, bridging monodentate and bidentate [10]; (d) tris-monodentate [13–17]; (e) tris-chelating [14,18–21]; (f) tris-bidentate [22]. It is necessary to note that these modes can be combined in a crystal structure.

Nickel centers atom prefers coordination number six and thus its coordination sphere must be completed by other ligands. Btc anion and water molecules functioning as ligands are reported in [23].

The pyridines, polyfunctional alcohols or 4-picoline were used in combination with btc anion and their structures were solved in [24–28]. Prior et al. have used bridging ligands 4-aminopyridine and 4,4′-bipyridine for the preparation of polymeric complexes [29,30]. Tetraaza and hexaazamacrocylic ligands in combination with btc and their structures are also known [31–35]. In our previous work we have prepared and characterized series of nickel and copper complexes with a combination of N-donor ligands or Schiff bases with btc anion [36]. Molecular structure of $[Cu_3(mdpta)_3(btc)](ClO_4)_3 \cdot 4H_2O$ (mdpta = *N*,*N*-bis-(3-aminopropyl)methylamine) was solved. There is a btc^{3-} bridge connecting three copper atoms in tris-monodentate mode. Coordination sphere of central atoms is completed by three N atoms of mdpta, forming deformed square plane.

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In this paper, we report on the preparation of the first nickel(II) trinuclear complex with 1,3,5-benzenetricarboxylate bridge. We have used bulky pmdien ligand to prevent the formation of a polynuclear complex and from X-ray study follows that the complex possesses deformed coordination sphere of the nickel(II) ion centers.

2. Experimental

2.1. Materials and methods

Safety note: *Caution*! Perchlorate salts of metal complexes with organic ligands are potentially explosive. Even small amount of these materials should be handled with great caution.

The chemicals and solvents were supplied from Aldrich and Lachema (Czech Republic). The C, H, N analyses were carried out on an EA 1108 instrument (FISONS). IR spectra were recorded on a Specord M 80 (Carl Zeiss, Jena).

Magnetic susceptibility measurements in the temperature range of 1.8–300 K were carried out on powdered sample, at the magnetic field of 5 kG using a Quantum Design SQUID Magnetometer (type MPMS-5). The correction for diamagnetism was calculated using Pascal's constants as -996×10^{-6} m^3 mol^{-1}, whereas the temperature independent paramagnetism of the Ni^{2+} centers was calculated as 220×10^{-6} cm^3 mol^{-1} [37]. The effective magnetic moment per nickel(II) atom was calculated from the equation $\mu_{eff} = 2.83\sqrt{\chi_M T}$ B.M., where χ_M is the molar magnetic susceptibility corrected for diamagnetism.

2.2. Synthesis of $[Ni_3(pmdien)_3(H_2O)_3(btc)](ClO_4)_3 \cdot 4H_2O$

Pmdien (0.42 cm^3, 2 mmol) was added to a solution of $Ni(ClO_4)_2 \cdot 6H_2O$ (0.74 g, 2 mmol) in ethanol (50 cm^3). A solution of $btcH_3$ (0.15 g, 1 mmol) in water (10 cm^3) neutralised with KOH (0.17 g, 3 mmol) was slowly added to the stirred brown solution.

Table 1
Crystal data and structure refinement for SC-2-1a

Empirical formula	$C_{36}H_{86}Cl_3N_9Ni_3O_{25}$
Formula weight	1327.62
Temperature (K)	173(2)
Wavelength (Å)	0.71073
Crystal system	monoclinic
Space group	$P2_1/c$
Unit cell dimensions	
a (Å)	11.7911(4)
b (Å)	30.7753(11)
c (Å)	17.0110(6)
α (°)	90
β (°)	107.637 (1)
γ (°)	90
Volume (Å^3)	5882.7(4)
Z	4
Density (calc.) (Mg/m^3)	1.499
Absorption coefficient (mm^{-1})	1.170
$F(000)$	2800
Crystal size (mm^3)	0.78 × 0.47 × 0.38
Theta range for data collection (°)	1.82–33.15
Index ranges	$-17 \leqslant h \leqslant 18$, $-46 \leqslant k \leqslant 45$, $-26 \leqslant l \leqslant 26$
Reflections collected	107 680
Independent reflections (R(int))	21 349 (0.0280)
Completeness to theta (%)	31.00° (100.0%)
Absorption correction	multi-scan
Maximum and minimum transmission	0.6649 and 0.4623
Refinement method	full-matrix least-squares on F^2
Data/restraints/parameters	21 349/9/553
Goodness-of-fit on F^2	1.012
Final R indices [$I > 2$sigma(I)]	$R_1 = 0.0385$, $wR_2 = 0.1080$
R indices (all data)	$R_1 = 0.0454$, $wR_2 = 0.1112$
Largest difference in peak and hole (e Å^{-3})	0.742 and −0.457

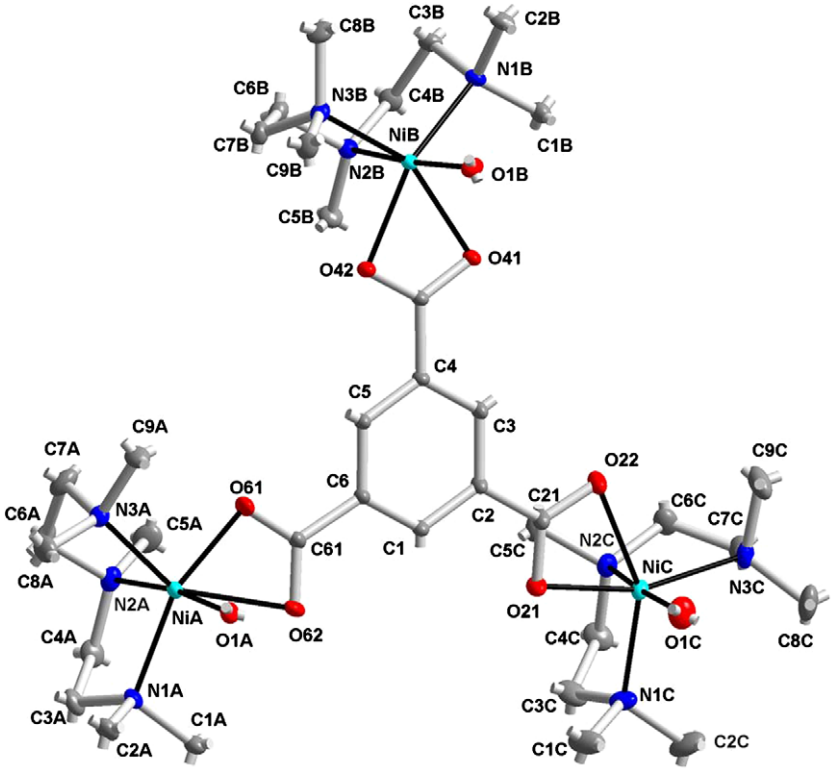

Fig. 1. Numbering scheme for $[Ni_3(pmdien)_3(btc)(H_2O)_3](ClO_4)_3 \cdot 4H_2O$ with atomic displacement ellipsoids drawn at 30% probability level. Hydrogen atoms are omitted for clarity.